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LEAD-FREE PAINT COATINGS FOR GLASS ARTICLES

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The effect of binders on the quality of paint coatings based on lead-free enamels and meeting the requirements of standard TU RB 100029049.030 is considered. It is established that enamel compositions can be prepared using 20% solution of oxyterpene resin in turpentine and 2% alcoholic solution of Na-carboxymethyl cellulose of grade 7MF. The use of an aqueous solution of dextrin as a binder deteriorates the quality of enamel coatings: it produces color modifications, loss of luster, and formation of crackle.

Enamel composites for decorating glass articles are stabilized colloid systems consisting of two main components: a solid-phase filler and a binder. The solid-phase filler in decorating glass articles is represented by a finely dispersed mixture of low-melting glass with colorant agents. The binder, which, as a rule, contains a film-forming agent, a solvent, and a plasticizing agent, envelopes the powdered enamel particles providing strong adhesion of the film to the unfired surface that has to be painted. As a consequence, a continuous solid elastic film is formed. The binders used in the silicate industry include turpentine oil, products of the wood-chemical industry (such as polyterpenes, oxyterpene resin, oxypolymers, colophony), dextrin, water-soluble polymers such as polyvinyl alcohol (PVA), and carboxymethyl cellulose (Na-CMC) [1 – 3]. The binding agents used in enamel composites have to decompose, volatilize, and burn during the firing of enamel coatings on glass before the enamel starts melting. Otherwise, reactions between the products of binder decomposition and enamel components, as well as resulting compounds may have a substantial effect on the properties of enamel coatings in firing: modify color, deteriorate their luster and adhesion, increase the firing temperature.

The purpose of our study is to investigate the effect of binders on the quality of paint coating based on lead-free enamels and meeting the requirements of TU RB 100029049.030 standard.

The solid-phase filler in our study was a finely milled (fraction below 40 μm) lead-free enamel dried for 1 h at the temperature of 100 ± 5°C and containing 95% low-melting glass and 5% chromium oxide pigment. The main components in the synthesis of low-melting glass were oxides of alkali metals, silicon, boron, barium, zinc, titanium, phosphor, and aluminum [4]. The following binders were used: 20% oxyterpene resin solution (TU 81-05-69–69) in turpentine, 2% alkali solution of Na-CMC of grade 7MF and 50% aqueous solution of dextrin. To prepare experimental compositions, the powdered enamel in a jasper mortar was mixed with particular binders in the ratio of 70 : 30. Enamel compositions were applied with a brush on a soda-lime glass substrate and fired in a muffle furnace in an oxidizing gaseous atmosphere at a temperature of 580°C with a 30 min exposure. Fired enamel coatings that had good luster, prescribed color, and no crackle were accepted as the reference standard.

The diffraction patterns of samples were recorded using a DRON-3 diffractometer (CuK_α radiation, Ni filter), differential thermal analysis was performed in corundise crucibles using a MOM derivatograph with the temperature rise rate of 10 K/min on a 800 mg sample. The reference standard for this analysis was calcined aluminum oxide of the "chemically pure" grade.

The x-ray diffraction analysis of powdered enamel does not identify any new phases (Fig. 1, curve *1*). The samples contain a single phase, namely chromium oxide. The DTA curve of the enamel has one endothermic effect with a maximum at 485°C caused by the start of the sample softening (Fig. 2*a*). The complete spreading of the enamel occurs at 600°C.

The derivatogram of dextrin has two clearly expressed endothermic effects with maxima at 132 and 195°C and two exothermic effects with peaks at 292 and 565°C accompanied by a weight loss of the sample (Fig. 2*b*). The data on weight variation under heating indicate that decomposition of dextrin proceeds in three stages. At the first stage (up to 200°C) the sample loses 50% weight, which approximately corresponds to the theoretical water content in the initial material, at the second stage (200 – 320°C) the inflammation of dextrin and its weight decrease by a further 20% take place,

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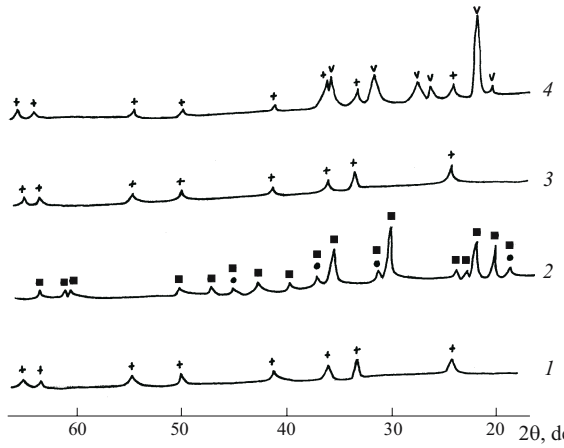

Fig. 1. X-ray patterns of samples heat-treated for 1 h at 580°C: *1*) powdered enamel containing flux and chromium oxide pigment; *2 – 4*) composites based on enamel combined with 50% dextrin solution, 2% solution of Na-CMC, and 20% solution of oxyterpene resin, respectively; +) Cr_2O_3; **v**) α-SiO_2; ●) $ZnAl_2O_4$; ■) $NaZn_{0.8}Cr_{0.2}(PO_4)$.

and at the third stage (320 – 600°C) gradual volatilization of the products of heating occurs. The total weight loss at 600°C is equal to 100%.

The shape of the thermogram of the enamel composition based on 50% dextrin solution dried at room temperature (Fig. 2*c*) is similar to the thermogram in Fig. 2*b* but differs by the additional endothermic effects with maxima at 500 and 580°C and a wide exothermic effect within a temperature interval of 540 – 570°C with a peak at 565°C. These effects are caused by the start of enamel softening and also by the chemical processes occurring in glass within the specified temperature interval between the enamel components and the products of decomposition of dextrin with the formation of solid solutions of the spinel type, which agrees with the data of x-ray phase analysis and the results in [5, 6]. Thus, x-ray phase analysis of the composition based on dextrin and enamel registered the formation of new phases, i.e., spinels of the compositions $NaZn_{0.8}Cr_{0.2}(PO_4)$ and $ZnAl_2O_4$, whereas chromium oxide is absent (Fig. 1, curve *2*). Based on the DTA data, the weight losses (up to 18%) keep growing up to a temperature about 570°C. The enamel composition is high-melting, since the softening temperature and complete spreading temperature increase by about 25°C.

It should be noted that enamel coatings fired at 580°C are colored black, instead of green in the reference standard, have cracks, and do not have luster. The reason for the changed coating color is presumably carbon that partly persists in the melt and the reason for the higher melting point is the formation of spinels.

The differential curve of the enamel composition where the binder is by 2% alcoholic solution of Na-CMC of grade 7MF has two endothermic effects with maxima at temperatures of 165 and 485°C and an exothermic effect with a peak

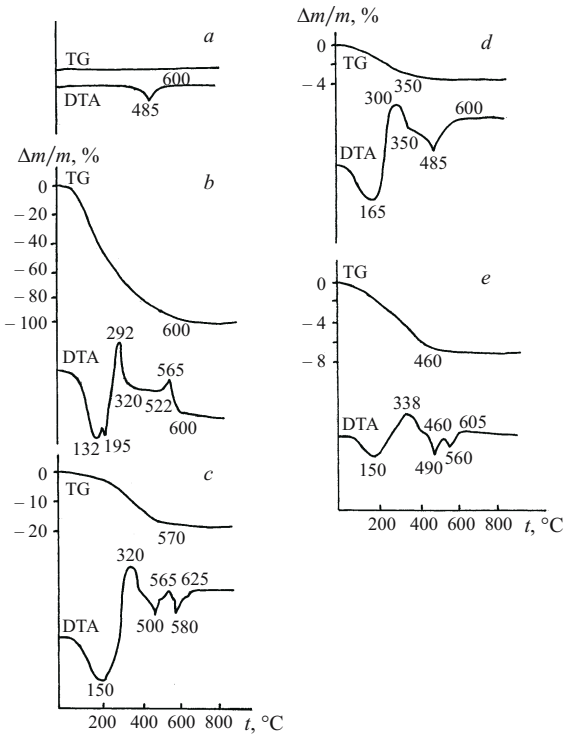

Fig. 2. Results of integrated thermal analysis of samples: *a*) enamel; *b*) dextrin; *c*, *d*, and *e*) composites based on enamel combined with 50% dextrin solution, 2% Na-CMC, and 20% solution of oxyterpene resin, respectively.

at 300°C. The first endothermic effect corresponds to the release of water vapor and the second one to glass melting (Fig. 2*d*). The complete decomposition of Na-CMC occurs within the temperature interval of 250 – 350°C. The total weight loss at a temperature of 350°C is 3%. X-ray phase analysis does not identify any new phases or compounds and registers only the presence of the chromium oxide phase (Fig. 1, curve *3*).

The color and luster of fired enamel coating based on the specified composition is green, same as in the reference standard, moreover, there is no crackle.

The differential curve of the enamel composition based on 20% oxyterpene resin solution in turpentine (Fig. 2*e*) has clearly expressed endothermic effect with a maximum at 150°C and exothermic effect with a peak at 338°C, both accompanied by a weight loss. At a temperature above 460°C the weight of the sample stops changing, which points to the complete decomposition of the binder. Under further heating, two endothermic effects are registered with maxima at 490 and 560°C. The first effect is related to glass softening and the second one to the reversible phase transformation of SiO_2 modifications α ⇄ β. According to x-ray phase analysis, a small quantity of α-SiO_2 is formed in samples heat-treated at 580°C (Fig. 1, curve *4*). It is known [7] that the phase transformation of SiO_2 modifications α ⇄ β occurs at the temperature of 560°C.

The color and luster of enamel coatings fired at 580°C based on the specified compositions correspond to the color and luster of the reference standard.

Thus, slip compositions based on lead-free enamel that meet the requirements of standard TU RB 100029049.030 can be prepared using 20% solution of oxyterpene resin in turpentine and 2% alcohol solution of Na-CMC of grade 7MF. An aqueous dextrin solution used as a binder inevitably deteriorates the quality of enamel coatings resulting in color modification, loss of luster, and formation of crackle.

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